THE EFFECT OF ORGANIC MATTER ON THE PRECIPITATION OF PHOSPHORUS AS AMMONIUM PHOSPHOMOLYBDATE

A THESIS

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by

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APPROVED

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INTRODUCTION

Practically all of the methods for the determination of phosphorus require a preliminary separation as ammonium phosphomolybdate, the ideal composition of which is $(NH_4)_3PO_4 . 12MoO_3 . 2HNO_3 . H_2O$.[1] Since it is difficult to form a precipitate of this composition,[1] numerous procedures for the subsequent treatment of the ammonium phosphomolybdate have been proposed. Extensive studies of the formation of this precipitate have been made, resulting in many modifications of this method as originally proposed by Sonnenschein.[2]

Although the umpire method of analysis for phosphorus consists in its final separation as magnesium ammonium phosphate and ignition to magnesium pyrophosphate, the Pemberton Method is now widely used due to the much shorter time required. Thus, studies on the interferences in the formation of the ammonium phosphomolybdate are of prime importance, since accurate results depend on the formation of a pure precipitate of definite composition.[1]

Previous investigators have differed widely in the results obtained from a study of the effects of organic matter on the precipitation of phosphorus as ammonium phosphomolybdate.

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1) Hildebrand & Lundell: Applied Inorg. Anal.,p560

2) Treadwell & Hall: Analytical Chem.,7th Ed,p281

Hundeshagen[1] was one of the first to point out that the presence of polybasic organic acids, such as oxalic and tartaric, prevent entirely the formation of this precipitate. Fresenius[2] states that certain substances such as tartaric acid and other reducing organic compounds have a disturbing effect on the reaction, that[3] the precipitation of phosphorus as ammonium phosphomolybdate from solutions containing organic matter is not quite complete, and the results are too low. Lundell, Hoffman, and Bright[4] states that the precipitation is retarded by some organic compounds. Kolthoff and Sandell[5] seem to agree with Fresenius, for they claim that organic substances such as oxalates and tartrates may interfere with the formation of the ammonium phosphomolybdate by forming fairly stable complexes with the molybdate, thus reducing the active concentration of this reagent.

Numerous studies have been made on complex compound formation between molybdic acid and organic compounds. However, most of this work was carried out using sodium or ammonium molybdate and malic or tartaric acid.[6] A survey of these re-

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1) Daniel&Griffin: Unpublished Thesis, Ga-Tech, 1933

2) Fresenius: Qual. Chem. Anal., 17th. Ed., p145

3) Fresenius: Quant. Chem. Anal., Vol.11, 6th. Ed., p527

4) Lundell, Hoffman, & Bright: Anal. of Iron & Steel, p212

5) Kolthoff & Sandell: Quant. Inorg., p

6) Chem. Abs., 2, 2658,(1908); 8, 666,(1914); 16, 2088,(1922); 19, 865,(1925); 20, 1184, 2940,(1926); 23, 1584,(1929).

ferences reveals that these investigators' observations gave evidence of complex formation, but they differed as to the composition. Britton and Jackson[1] obtained evidence from rotation experiments of the formation of the complex, Na_2MoO_3. $C_4H_4O_6$, which is stable in neutral and acid solution. They also found that the complex formed with a greater proportion of the sodium molybdate if this compound was added in excess. Reinbach and Wintgen[2] have made a study of and shown that malic, lactic, glycolic, tartaric, citric, quinic, and mandelic acids form complex compounds with molybdic acid. They also obtained results which may indicate the formation of complex compounds between propionic, succinic, phenylacetic, phenylglycolic, or acetic acids with molybdic acid. The method used was based on the variation of the volume and refraction of the liquid from the additive property. Fernandes[3] obtained data to favor the hypothesis that MoO_3 combined with various hydroxy acids with the elimination of water and the formation of a complex.

However, there are others who present an entirely different view. Thus, Lord and Demorest[4] say that the bad results obtained in the analysis of phosphorus and attributed to organic matter are probably due to the fact that the phosphorus had not

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1) J. Chem. Soc., ___, 998,(1934)

2) Z. Physik, Chem., 74, 233,(1910)

3) Chem. Abs., 18, 1252, (1924)

4) Lord & Demorest: Metallurgical Analysis, 5th Ed., p46

all been converted to the tribasic state(phosphate ions). They admit, however, that solutions of certain organic acids, such as tartaric and oxalic, dissolve the ammonium phosphomolybdate to some extent. Lundell and Hoffman[1] state that large amounts of organic matter interfere in the precipitation of ammonium phosphomolybdate and that small quantities (0.1 to 0.3 gram) of such substances as citric or tartaric acid are without appreciable effect. Maderna[2] contradicts the statements of Hundeshagen by claiming that organic substances, especially such acids as succinic, malonic, d-tartaric, benzoic, oxalic, acetic, citric, salicylic, and phthalic, do not prevent the precipitation of ammonium phosphomolybdate if enough nitric acid is present. He also claims that quantitative precipitation can be obtained in the absence of nitric acid if certain proportionalities exist between the ammonium phosphomolybdate and organic acids, and that the complexes formed between the organic compounds and the molybdic acid or perhaps phosphoric acid are quite stable.

In general, organic matter is regarded as objectionable in practically all analytical methods, although in some procedures the addition of certain organic compounds is recommended. Ware[3] states "In qualitative and quantitative analysis, organic matter

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1) Lundell & Hoffman: Ind. and Eng. Chem., 15, 44,(1923)

2) Chem. Abs., 5, 1379,(1911)

3) Ware: Chem. of Colloidal State, p214

must be removed on account of its stabilizing action before precipitation can be made". Alexander[1] attributes certain inhibitions of precipitation to the formation of colloidal non-filterable sols due to the presence of such substances as citrates, tartrates, organic extractives, etc. Organic matter[1] may act (a) by partially or totally preventing the formation of precipitates;[2] (b) by preventing the satisfactory filtration of the precipitate when formed;[3] and (c) by rendering the precipitate difficult to wash and purify.[4]

Daniel and Griffin[5] have made an extensive study of the effect of a number of organic compounds (ethanol, propanol, n-, tertiary, and iso-butanol; acetic, propionic, n-, and iso-butyric, glycolic, oxalic, tartaric, citric, and succinic acids; ethylene glycol, acetone, and sucrose) on the precipitation of phosphorus as ammonium phosphomolybdate. They obtained discrepancies in the amounts of ammonium phosphomolybdate precipitated in the presence of small amounts of organic matter that indicate interference phenomena. Their results further reveal that practically all organic compounds studied will completely prevent the precipi-

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1) Alexander: Colloid Chemistry, p286

2) Yoshimoto, J. Soc. Chem. Ind., 27, 952, (1908)

3) Hampton, J. A. C. S., 30, 805, (1908)

4) Duclaux, J. Soc. Chem. Ind., 25, 866, (1906)

5) Daniel and Griffin, Unpublished Thesis, Ga-Tech, (1933)

tation. In some cases, even the yellow color was destroyed, while in others yellow solutions were obtained when precipitation was prevented.

SOLUTIONS AND REAGENTS

PHOSPHATE SOLUTION[1]

The phosphate solution was prepared by dissolving approximately 1.3 grams of $Na_2HPO_4.12H_2O$, C.P., in one liter of distilled water.

AMMONIUM NITRATE

Eight grams of ammonium nitrate, C. P., were dissolved in distilled water to make 25 cc of solution. Generally these solutions were made up in 250 cc volumetric flasks, but were never kept over two or three days before using.

ORGANIC COMPOUNDS

The organic compounds were either Eastman or C. P. chemicals of a reliable brand. The liquids were added to the sample by means of a calibrated burette, while the solids were weighed and transferred to the flask.

MOLYBDATE SOLUTION[1]

100 grams of 85% molybdic acid, C. P., were dissolved in a solution containing 144 cc of ammonium hydroxide (sp.gr.0.90) and 270 cc of distilled water. This solution was slowly poured with constant stirring into another solution consisting of

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1) Daniel and Griffin, Unpublished Thesis, Ga-Tech, 1933

570 cc of nitric acid (sp.gr. 1.42) and 1150 cc of distilled water. This solution was allowed to stand for twenty-four hours and then decanted from any sediment into a glass-stoppered bottle.

POTASSIUM NITRATE SOLUTION

A 2% solution of potassium nitrate, C. P., was prepared by dissolving 20grams of the salt in a liter of solution.

TENTH-NORMAL SODIUM HYDROXIDE SOLUTION

Five grams of sodium hydroxide, C. P., were rinsed off with distilled water to remove any carbonates, and then dissolved in 100 cc of distilled water. One cc of a saturated solution of barium hydroxide was added, and the barium carbonate which formed was filtered off, the solution passing into a glass bottle. This solution was diluted to a liter with recently boiled but cooled distilled water, and then diluted to sufficient volume to give an exactly 0.1 normal solution, being standardized against potassium acid phthalate, using phenolphthalein as indicator. It was generally desired to prepare several liters at one time, and then proportional quantities were used. The solution was kept in a glass bottle fitted with a two-hole rubber stopper containing a soda-lime absorption tube and a delivery tube which was connected to the burette. This solution was repeatedly checked against 0.1 normal hydrochloric acid and also against potassium acid phthalate.

TENTH-NORMAL HYDROCHLORIC ACID SOLUTION

Concentrated hydrochloric acid, C. P., was diluted to an approximately 0.1 normal solution, using recently boiled but cool distilled water. This solution was made exactly 0.1 normal by standardizing against 0.1 normal sodium hydroxide, using phenolphthalein as indicator.

ANALYTICAL PROCEDURES

PROCEDURE I

In order to determine the effect of various organic compounds when present in different amounts on the precipitation of phosphorus as ammonium phosphomolybdate, this procedure was used. This is essentially the same procedure which was employed by Daniel and Griffin.[1]

Twenty-five cc of the phosphate solution were pipetted into a 500 cc erlenmeyer flask. To this were added 25 cc of a solution containing 8 grams of ammonium nitrate, then the organic matter, and then enough distilled water to make 100 cc of solution (unless otherwise noted in the results). Fifty cc of freshly filtered molybdate solution were added, and the flask immediately shaken in a mechanical shaker for exactly thirty minutes. The liquid was then immediately decanted through a quantitative filter paper. The precipitate remaining in the flask was washed five times by decantation with 15 cc portions of potassium nitrate solution, transferred to the filter paper and again washed five times with 15 cc portions of the potassium nitrate solution. The tenth

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1) The frequent reference to the work of Daniel and Griffin as hereafter referred to may be found in : Daniel and Griffin, Unplublished Thesis, Georgia-Tech, (1933)

wash filtrate was tested with blue litmus paper to insure removal of all nitric acid.

The filter paper containing the ammonium phosphomolybdate was transferred to the original flask, and fifty cc of freshly boiled but cool distilled water added. More then enough of the 0.1 normal sodium hydroxide solution to dissolve all of the precipitate was added. After allowing about five minutes to insure complete solution of the precipitate, the excess base was titrated with the 0.1 normal hydrochloric acid, using phenolphthalein as indicator.

PROCEDURE II

Lundell, Hoffman, and Bright[1] claim that some organic compounds retard the precipitation of ammonium phosphomolybdate. The authors also obtained indications of such retardation by allowing the filtrates from the analyses (Procedure I) to stand overnight for observation. Thus the following procedure was employed in an attempt to determine whether the precipitation of the ammonium phosphomolybdate was prevented or merely delayed in the presence of organic matter.

Twenty-five cc of the phosphate solution were pipetted into a 500 cc erlenmeyer flask. To this were added twenty-five cc of a solution containing 8 grams of ammonium nitrate, then the organic matter, and then enough distilled water to make

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1) Lundell, Hoffman, & Bright: Anal. of Iron & Stell, p212

100 cc of solution. Fifty cc of freshly filtered molybdate solution were added, and the flask well stoppered and allowed to stand for ten days (unless otherwise noted). The liquid was then decanted through a quantitative filter paper and washed five times with 15 cc portions of the 2% potassium nitrate solution. The filtrate, which is designated in the results as filtrate A, was received in a 250 cc beaker, covered and set aside for observation. The wash water portion of the filtrate was discarded. The precipitate on the filter paper, which is designated as precipitate A, was dissolved in 15 cc of warm 1:1 ammonium hydroxide, the solution passing into the original flask. The filter paper was then washed with two 15 cc portions of 1:20 ammonium hydroxide, and then thoroughly with warm water. The solution was cooled, made slightly acid to litmus with 1:3 nitric acid, and then diluted to 115 cc with distilled water. Thirty-five cc of the molybdate solution were added, and the sample shaken for exactly thirty minutes in the mechanical shaker, and then continued according to Procedure I. The precipitate and filtrate from this second filtration were designated as precipitate B and filtrate B.

PROCEDURE III

It was shown by Daniel and Griffin and then further confirmed by the present authors (Procedure I) that certain organic compounds prevented the precipitation of ammonium phosphomolybdate, but gave a yellow solution from which a precipitate formed on standing. Since this is suggestive of the formation

of a colloidal solution, it was deemed advisable to attempt dialysis of these yellow solutions.

The solution was first filtered through a quantitative filter paper. Fifteen cc of the filtrate were poured into the dialysis membrane, which was in turn clamped so as to remain securely in the center of a slightly larger test tube. The test tube was then filled with distilled water to the same level as the solution within the membrane. After 24 hours the solution on the outside of the membrane was tested for phosphorus.

The same method of dialysis was also employed using those colorless solutions which were obtained when certain organic compounds prevented the precipitation of the ammonium phosphomolybdate.

PROCEDURE IV

The purpose of this experiment is to further verify the results of Procedure III. It is similar, except that the solutions after being filtered through a quantitative filter paper were then filtered through an unglazed porcelain filter crucible. The crucible was examined for a precipitate and the color of the filtrate was noted.

MICROSCOPIC EXAMINATION

The microscopic examination was made under the oil immersion. Approximately one-tenth cc of the liquid to be examined was placed on a cover glass, inverted and lowered over

the cavity of a hollow ground slide and ringed with vaseline. This was immediately placed under the oil immersion lens(950), and carefully examined.

LOWERING OF THE FREEZING POINT DETERMINATIONS

Studies were made of the lowering of the freezing point in an attempt to determine the formation of complex compounds in solution. A critical survey of the literature reveals that a large number of organic compounds are capable of combining with the molybdate ion or molecule, forming fairly stable complexes.

The method employed was that as outlined by Daniels, Mathews, and Williams[1] with a few modifications to suit the conditions. The materials were weighed directly into the weighing bottle, then twenty cc of distilled water added, and weighed again. The sample was allowed to stand, with occasional shaking, for several minutes or until solution was complete. It was then transferred to the freezing point apparatus with a funnel.

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1) Daniels, Mathews, & Williams: Experimental Physical Chem., P,55

ACETIC ACID

The effect of certain concentrations of acetic acid on the precipitation of phosphorus as ammonium phosphomolybdate was determined according to Procedure I, with the following results:

Sample no.	Mols acetic acid	Mols P_2O_5 not ppted.x 10^6
1	0.200	0.22
2	0.200	0.41
3	0.400	0.07
4	0.400	-0.02*
5	0.600	1.39
6	0.600	1.71
7	0.800	42.22
8	0.800	41.72
9	0.900	48.85
10	0.900	48.85

The number of mols of P_2O_5 in each sample was 48.85 x 10^{-6}.

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* The negative sign frequently placed before the value in the results represents that more sodium hydroxide was required to dissolve the precipitate than when precipitated in the absence of organic matter. Thus, this is here expressed as excess mols of P_2O_5 precipitated from the sample.

Each of the filtrates from samples 1, 2, 3, and 4 were colorless and the precipitates were apparently normal. The filtrates from 5 and 6 were only slightly yellow, while those of 7 and 8 were distinctly yellow. The filtrates were allowed to stand overnight, and a small precipitate appeared in 5, 6, 7, and 8, although those in 5 and 6 were small and not characteristic. A precipitate also formed in 9 and 10 on standing overnight. This seemed to indicate that the acetic acid might merely be delaying the precipitation.

A number of analyses were made in the presence of acetic acid in which the final volume was 200 cc instead of 150 cc, but otherwise Procedure I was used. A few of the results are given below.

Sample no.	Mols acetic acid	Mols P_2O_5 not ppted.x 10^6
1	0.100	0.30
2	0.300	0.35
3	0.700	2.78
4	0.900	9.22
5	1.000	45.84
6	1.100	48.85

The number of mols of P_2O_5 in each sample was 48.85×10^{-6}. The results are similar to those given on the preceding page except that a larger amount of acetic acid was required to prevent precipitation. The filtrates from 1 and 2 were colorless, 3 showed a tinge of yellow, and 4 and 5 were distinctly yel-

low. A small precipate formed in 5 on dilution with wash water. Sample 6 was yellow and gave a yellow precipitate on standing overnight. Additional samples were run giving similar results, but marked discrepances were noted even in the presence of identical amounts of acetic acid.

It was found that better checks could be obtained if the time interval was exactly the same between each step in the procedure. This was probably due to the fact that more precipitate would form if a slightly longer time was allowed. However, as only one determination could be performed at a time, very few samples were run in this way.

As a result of these analyses, it seemed advisable to determine whether the precipitation was prevented or merely delayed in the presence of acetic acid. Therefore, several analyses were conducted according to Procedure II with the following results:

Sample no.	Mols acetic acid	Mols P_2O_5 not ppted.x 10^6
1	0.900	0.26
2	0.900	0.19

The number of mols of P_2O_5 in each sample was 48.85×10^{-6}. The original flasks were allowed to sit for eight days before filtering. Filtrates A showed a slight tinge of yellow, indicating that precipitation was not complete, but gave no further precipitation on standing for several days. Examination under the microscope revealed very few small yellow

particles. In each case precipitates A were apparently contaminated with molybdic acid. The filtrates B were colorless and the precipitates normal. These results indicate that acetic acid delays the precipitation of ammonium phosphomolybdate.

Small yellow precipitates were separated from a number of these yellow solutions by dialysis according to Procedure III. These solutions were always filtered through a quantitative filter immediately before placing them in the membrane. In no case was a test for the phosphate ion obtained in the outer tube.

A small yellow precipitate was also obtained when any of these yellow solutions were filtered through a crucible filter according to Procedure IV, but the filtrate was still yellow. However, it was apparently lighter in color than the original. Small yellow particles were observed in this filtrate when examined under the microscope.

The view that large amounts of acetic acid will delay or partially prevent the precipitation of ammonium phosphomolybdate by its stabilizing action, thus forming a colloidal solution, is further confirmed by the addition of larger quantities of ammonium nitrate or ammonium molybdate solution. There was always an increase in precipitation of the ammonium phosphomolybdate with increase of ammonium nitrate or increase of molybdate solution.

N-PROPIONIC ACID

A study was made of the effect of another fatty acid, n-propionic, on the precipitation of phosphorus as ammonium phosphomolybdate. The following results, which are similar to those of Daniel and Griffin, were obtained according to Procedure I:

Sample no.	Mols acid	Mols P_2O_5 not ppted. $\times 10^6$
1	0.100	0.08
2	0.100	0.36
3	0.200	0.40
4	0.200	0.11
5	0.300	1.28
6	0.300	1.50
7	0.400	1.94
8	0.400	2.50
9	0.500	49.11
10	0.500	49.11

The number of mols of P_2O_5 in each sample was 49.11×10^{-6}. Precipitates 1 through 8 were apparently normal, and the filtrates were colorless. On standing overnight, a small precipitate appeared in filtrates 5, 6, 7, and 8 and in samples 9 and 10.

In order to determine whether the precipitation was pre-

vented or merely delayed, several analyses were performed according to Procedure II. Filtrates A were slightly yellow, and the precipitates A were contaminated with molybdic acid. The following results were obtained:

Sample no.	Mols acid	Mols P_2O_5 not ppted.x 10^6
1	0.500	-0.24
2	0.500	0.09

The number of mols of P_2O_5 in each sample was 49.11×10^{-6}. Filtrates B were colorless and the precipitates were apparently normal. The higher value of sample 1 may be due to co-precipitation of molybdic acid. However, it seems reasonable to assume that the value should be lower than the amount actually present, for probably the first precipitation was not complete as shown by the yellow color of filtrates A. When these filtrates were examined under the microscope a few small yellow particles were observed, further substantiating this assumption.

This concentration of n-propionic acid (0.5 mols per 150 cc of solution) does not not have a solvent action on the ammonium phosphomolybdate. This was shown by adding 0.5 mol of the acid to a sample in which the ammonium phosphomolybdate had been precipitated normally, and then shaking for thirty minutes and continuing according to Procedure I. Normal results were obtained.

The yellow solutions obtained when the precipitation was

prevented by the n-propionic acid gave similar results on dialysis and on filtration through the filter crucible as those containing acetic acid.

The investigations of Reinbach and Wintgen[1] point out the possibility of the formation of a complex in mixed solution of propionic acid and molybdic acid. The nature of the effect of propionic acid on the precipitation of phosphorus as ammonium phosphomolybdate does not indicate such a formation, unless the complex is unstable. In order to check this, a study was made of the lowering of the freezing point of mixed solutions of sodium molybdate and propionic acid. These values were compared with those obtained by using sodium molybdate only. The following is expressed as the number of mols of the compound per 1000 grams of water.

Mols sodium molybdate	Lowering of F. P.
25.50×10^{-3}	0.142
52.63	0.258
89.81	0.424
118.80	0.562
149.90	0.699
189.90	0.861

Mols sodium molybdate	Mols propionic acid	Lowering of F. P.
27.92×10^{-3}	43.61×10^{-3}	0.168

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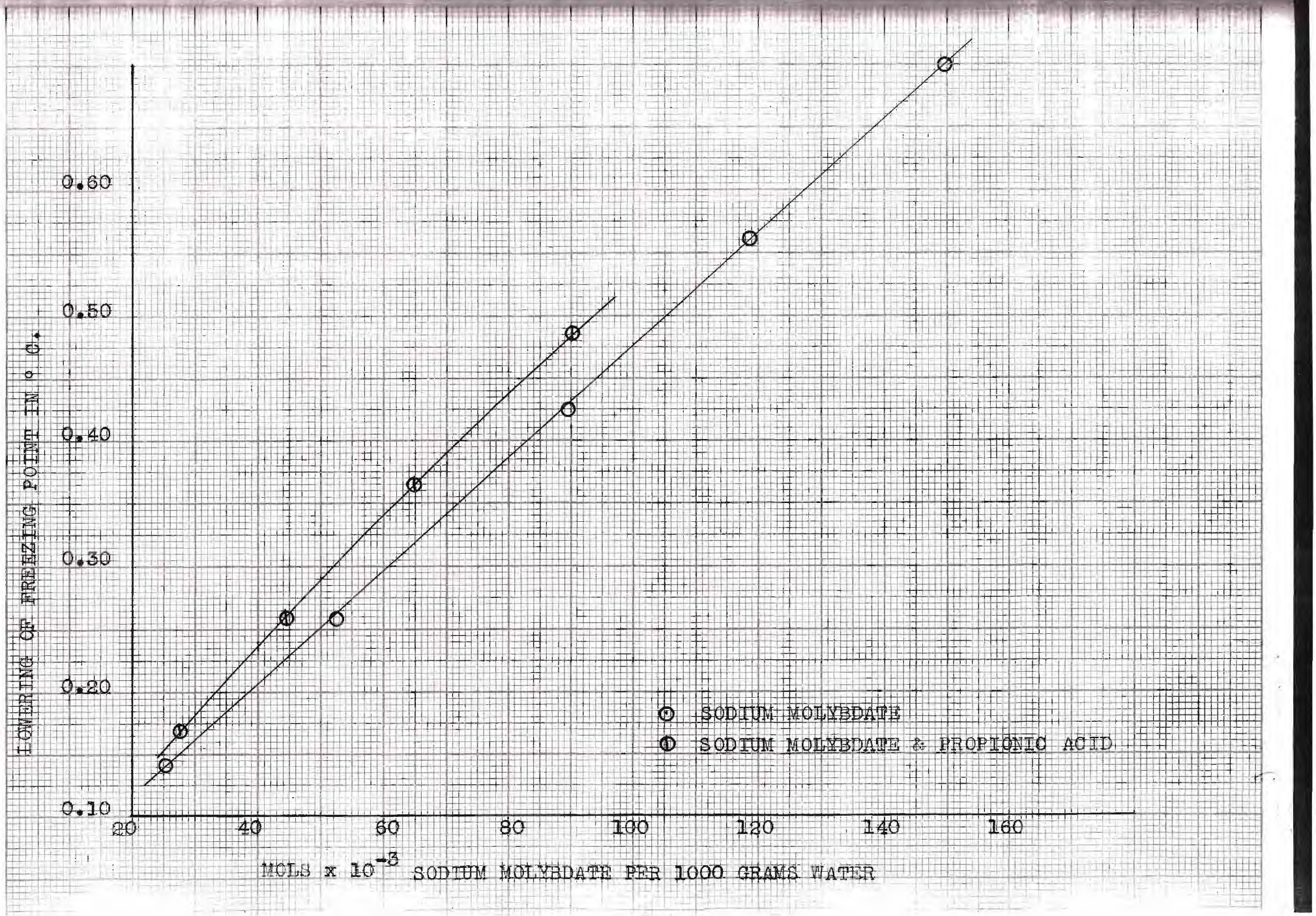
1) Loc. cit.

Mols sodium molybdate	Mols propionic acid	Lowering of F. P.
44.78	51.66	0.260
64.77	75.31	0.365
90.24	97.86	0.485

These values are plotted as shown on the following page. The upper curve represents the lowering of the freezing point of solutions containing the number of mols of sodium molybdate as represented, but also contains an approximately equal number of mols of propionic acid. The values represented on the lower curve are for sodium molybdate alone. These curves show that the addition of propionic acid to a solution of sodium molybdate (mol for mol, approximately) does increase the lowering of the freezing point. However, the values are slightly less than additive indicating a smaller number of particles in the solution. Although this small decrease in the lowering may be due to the effect of concentration or presence of the propionic acid, it may be due to formation of complex ions.

If a complex is formed in the solution between the propionic acid and the molybdate, it is evidently unstable under the conditions in which the ammonium phosphomolybdate is precipitated. The authors' investigations indicate that the ammonium phosphomolybdate is formed, but is not precipitated due to the stabilizing action of the propionic acid.

However, if a complex is formed, it might in some way account for the low values obtained when the precipitation occurs in the presence of small amounts of propionic acid.


LOWERING OF FREEZING POINT IN ° C.
0.60
0.50
0.40
0.30
0.20
0.10
20
40
60
80
100
120
140
160
MOLS x 10^{-3} SODIUM MOLYBDATE PER 1000 GRAMS WATER
SODIUM MOLYBDATE
SODIUM MOLYBDATE & PROPIONIC ACID

NORMAL-BUTYRIC ACID

Daniel and Griffin have shown that 0.273 mols of normal butyric acid completely prevented the precipitation of 48.44 x 10^{-6} mols of P_2O_5 as ammonium phosphomolybdate when analyzed according to Procedure I. These experiments were not repeated, but the authors found that even 0.250 mols of n-butyric acid prevented the precipitation of 49.11 x 10^{-6} mols of P_2O_5. Daniel and Griffin, however, did not try the effect of this amount of acid.

The analyses of two samples were determined as given in Procedure II. Even after standing for ten days, the supernatant liquid was still yellow, but the precipitate in each was larger than normal due to co-precipitation of molybdic acid. The precipitate had a tendency to adhere to the walls of the flask and was in a very fine state of division. The filtrates A were also slightly yellow. Examination under the microscope showed these to contain small, yellow-appearing particles, which were only a few microns in diameter. A small amount of yellow solid was obtained on filtering through a porcelain filter crucible. The following data were obtained:

Sample no.	Mols of acid	Mols P_2O_5 not ppted.x10^6
1	0.250	1.19
2	0.250	0.93

The number of mols of P_2O_5 in each sample was 49.11 x 10^{-6}.

The yellow color of filtrates A was probably due to incomplete precipitation as indicated by the above results.

The ammonium phosphomolybdate is apparently insoluble in a solution of n-butyric acid, as shown by tests and results similar to those obtained with n-propionic acid.

These results indicate that the effect of n-butyric acid on the precipitation of ammonium phosphomolybdate is similar to that of the other two fatty acids (acetic and n-propionic). However, we are not justified in stating that all fatty acids cause a stabilizing effect on the ammonium phosphomolybdate, producing a colloidal solution, and thus delaying the precipitation. Daniel and Griffin have shown that certain concentrations of formic acid will react with the nitric acid, thus preventing further study. Due to the limited solubility of the other members of this series, only a restricted investigation of the effect of the fatty acids was possible.

ISO-PROPYL ALCOHOL

Analyses were not performed to determine the effect of small amounts of iso-propyl alcohol on the precipitation of phosphorus as ammonium phosphomolybdate. However, it was found that 0.260 mols of this alcohol would completely prevent the precipitation of 49.11×10^{-6} mols of P_2O_5 according to Procedure I. Similar samples were analyzed according to Procedure II with the following results:

Sample no.	Mols iso-propyl alcohol	Mols P_2O_5 not ppted. $\times 10^6$
1	0.260	0.70
2	0.260	0.42

The number of mols of P_2O_5 in each sample was 49.11×10^{-6}. The low results were probably due to incomplete precipitation in the presence of the alcohol, since filtrates A were slightly yellow. Examination of these filtrates under the microscope revealed small yellow particles. The precipitates A possessed a greenish tinge and were contaminated with molybdic acid. This color is not characteristic of ammonium phosphomolybdate and is probably due to reduction phenomena. The precipitates B were apparently normal and the filtrates colorless.

The addition of 0.260 mols of iso-propyl alcohol to a sample in which the ammonium phosphomolybdate had been precipitated normally, gave results similar to those with n-pro-

picnic acid.

The effects of large amounts of iso-propyl alcohol on the precipitation of phosphorus as ammonium phosphomolybdate is similar to that of the fatty acids. However, in addition to the stabilizing action, there is probably also reduction of a small amount of the molybdenum producing a greenish color.

TERTIARY BUTYL ALCOHOL

The study of the effects of different amounts of tertiary butyl alcohol on the precipitation of phosphorus as ammonium phosphomolybdate according to Procedure I gave the following results, which are in general agreement with those of Daniel and Griffin:

Sample no.	Mols t-butyl alcohol	Mols P_2O_5 not ppted.x10^6
1	0.100	-0.08
2	0.100	-0.89
3	0.200	0.12
4	0.200	-0.13
5	0.250	49.11
6	0.250	49.11

The number of mols of P_2O_5 in each sample was 49.11×10^{-6}. Each of the first four precipitates and filtrates appeared to be normal. No precipitates appeared in either of these filtrates on standing for twenty-four hours. Samples 5 and 6 were tightly stoppered and allowed to stand overnight. Precipitates formed, but in each case the filtrates were still yellow. Examination, under the microscope, of the filtrate from one of these samples revealed small yellow particles.

Since a precipitate formed in samples 5 and 6 on standing, several samples containing 0.250 mols of t-butyl alcohol were analyzed according to Procedure II. Filtrates A were slightly

yellow, and precipitates A were contaminated with molybdic acid. The following results were obtained:

Sample no.	Mols t-butyl alcohol	Mols P_2O_5 not ppted.x10^6
1	0.250	0.19
2	0.250	0.10
3	0.250	-0.24

The number of mols of P_2O_5 in each sample was 49.11×10^{-6}. Precipitates B were normal in appearance, and filtrates B were colorless. The only explanation which the authors can give for the higher value of sample 3 is the possible contamination of molybdic acid which was too strongly adsorbed to be removed with the wash solution.

These results show that the precipitation of the ammonium phosphomolybdate is delayed or partially prevented by the t-butyl alcohol. The low values of the first two samples and the yellow color of filtrates A indicate that the precipitation was not quite complete even after standing for ten days.

The results of analysis according to Procedure III and IV further indicate that tertiary butyl alcohol delays the precipitation of ammonium phosphomolybdate by its stabilizing action.

METHYL ETHYL KETONE

The following results were obtained according to Procedure I showing the effect of methyl ethyl ketone on the precipitation of phosphorus as ammonium phosphomolybdate.

Sample no.	Mols M. E. ketone	Mols P_2O_5 not ppted.x10^6
1	0.100	-0.02
2	0.100	-1.10
3	0.150	11.43
4	0.150	9.66
5	0.200	41.06
6	0.200	41.57
7	0.250	49.11
8	0.250	49.11

The number of mols of P_2O_5 in each sample was 49.11×10^{-6}. The precipitates from samples 1 and 2 were apparently normal and the filtrates colorless. However, the filtrates from 3, 4, 5, and 6 were yellow, and the precipitates from 5 and 6 showed a brownish tinge. The beakers containing the filtrates, exclusive of the wash solution, were allowed to stand for twenty-four hours. During this time, a precipitate formed in 3, 4, 5, and 6, leaving the supernatant liquid colorless. Evidently a large portion of the methyl ethyl ketone had volatilized.

In order to determine whether the precipitation of the

ammonium phosphomolybdate was prevented or merely delayed in the presence of methyl ethyl ketone, several samples were analyzed according to Procedure II. Care was taken to avoid volatilization of the methyl ethyl ketone. After standing for two days the supernatant liquid above the precipitate appeared colorless. However, the samples were allowed to stand for four days before filtering. The precipitates A were only slightly contaminated with molybdic acid and the filtrates A were colorless. The following results were obtained:

Sample no.	Mols M. E. ketone	Mols P_2O_5 not ppted. x 10^6
1	0.250	0.04
2	0.250	0.09

The number of mols of P_2O_5 in each sample was 49.11 x 10^{-6}. These results as well as the colorless filtrates A indicate that the precipitations were complete. The small discrepancy in each case may be due to the second precipitation or to experimental error.

These results show that methyl ethyl ketone retards the precipitation of ammonium phosphomlybdate. The results obtained according to Procedure III and IV indicate that this organic compound delays the precipitation due to a stabilizing action on the ammonium phosphomolybdate. However, this stabilizing power does not seem to be as great as with the fatty acids and the alcohols.

METHYL ACETATE

The following results were obtained according to Procedure I showing the effect of methyl acetate on the precipitation of phosphorus as ammonium phosphomolybdate.

Sample no.	Mols methyl acetate	Mols P_2O_5 not ppted.x10^6
1	0.100	0.95
2	0.100	1.45
3	0.200	12.96
4	0.200	14.11
5	0.300	49.11
6	0.300	49.11

The number of mols of P_2O_5 in each sample was 49.11×10^{-6}. The precipitates from 1, 2, 3, and 4 were normal in color, but the filtrates were yellow. Precipitation was completely prevented in samples 5 and 6. However, on standing overnight, precipitates formed in samples 5 and 6, and smaller ones in the filtrates from the first four samples.

These results indicate that the precipitation was delayed or partially prevented by the methyl acetate, but no attempt was made to determine whether precipitation would be complete if a longer time were allowed.

ETHYLENE GLYCOL

Daniel and Griffin have studied the effect of ethylene glycol on the precipitation of phosphorus as ammonium phosphomolybdate. They found that 0.719 mols of this compound completely prevented precipitation in a solution containing 46.96 x 10^{-6} mols of P_2O_5. The authors have found using Procedure I that even 0.700 mols of ethylene glycol prevented the precipitation in a sample containing 49.11 x 10^{-6} mols of P_2O_5, but produced a yellow solution.

In order to determine whether the precipitation was prevented or merely delayed by ethylene glycol, several samples were run according to Procedure II. Filtrates A showed only a slight tinge of yellow, but precipitates A were contaminated with molybdic acid.

Sample no.	Mols ethylene glycol	Mols P_2O_5 not ppted.x10^6
1	0.700	0.85
2	0.700	0.74

The number of mols of P_2O_5 in each sample was 49.11 x 10^{-6}. Precipitates B and filtrates B were normal in appearance. The low results were probably due to incomplete precipitation as shown by the yellow color of filtrates A. Examination of one of these filtrates under the microscope revealed a few small, yellow particles.

The authors also obtained results which indicate that the ammonium phosphomolybdate is slightly soluble in a solution containing ethylene glycol, and may account for the low results given above. To two normal precipitations of ammonium phosphomolybdate were added 0.700 mols of this organic compound. Sample 1 was shaken for thirty minutes. Sample 2 was shaken for thirty minutes, allowed to stand for four hours, and again shaken for thirty minutes. Immediately after shaking, the analysis was continued according to Procedure I. The following results were obtained:

Sample no.	Mols ethylene glycol	Mols P_2O_5 in sol'n.x10^6
1	0.700	0.41
2	0.700	0.60

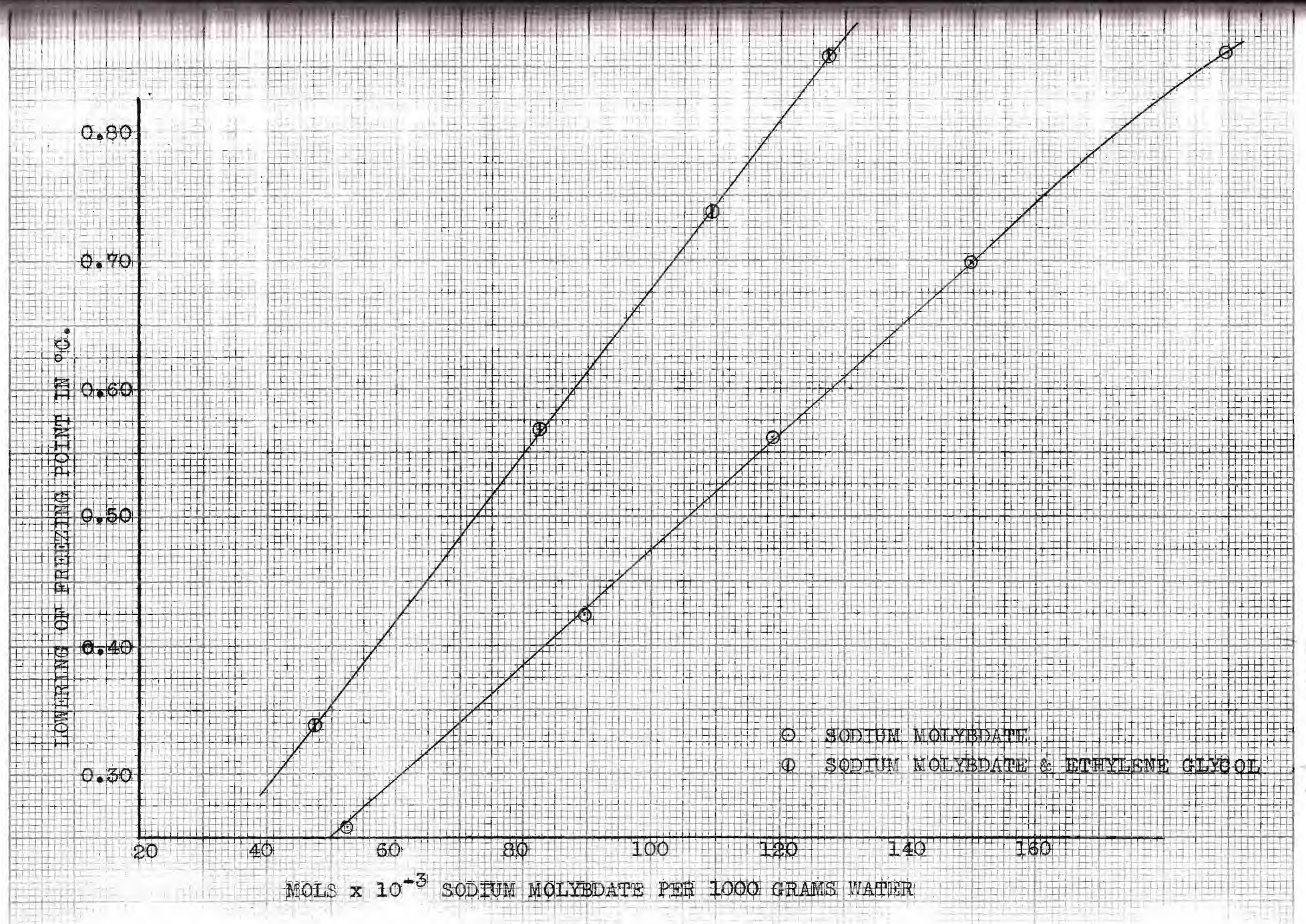
The number of mols of P_2O_5 in each sample was 49.11×10^{-6}. There was a slight tint of yellow in each filtrate. This may have been due to peptization.

The work of Daniel and Griffin showed that small amounts of ethylene glycol decreased the amount of ammonium phosphomolybdate that was precipitated. A possible explanation would be the formation of a complex ion or compound which would reduce the concentration of the precipitating agent. The following data were obtained on the lowering of the freezing point of solutions of sodium molybdate and ethylene glycol in an attempt to determine whether a complex was formed:

Mols Na_2MoO_4	Mols ethylene glycol	Lowering of F. P.
47.21×10^{-3}	53.48×10^{-3}	0.339
82.66	88.30	0.569
109.47	110.37	0.738
127.66	127.27	0.859

These values and those for sodium molybdate (page 20) are plotted on the following page. The upper curve represents the lowering of the freezing point of solutions containing the number of mols of sodium molybdate as represented on the abscissa, but also contains an approximately equal number of mols of ethylene glycol. The values represented on the lower curve are for sodium molybdate alone. These do not indicate the formation of complex compounds as the lowerings are additive.

The results indicate that ethylene glycol interferes with the precipitation of ammonium phosphomolybdate by its stabilizing action, forming a colloidal solution. The results obtained according to Procedure III and IV were similar to those with the fatty acids.


LOWERING OF FREEZING POINT IN °C.
0.80
0.70
0.60
0.50
0.40
0.30
20
40
60
80
100
120
140
160
MOLS x 10^{-3} SODIUM MOLYBDATE PER 1000 GRAMS WATER
SODIUM MOLYBDATE
SODIUM MOLYBDATE & ETHYLENE GLYCOL

GLYCEROL

The following results (Procedure I) show the effect of glycerol on the precipitation of phosphorus as ammonium phosphomolybdate.

Sample no.	Mols glycerol	Mols P_2O_5 not ppted.x 10^6
1	0.100	0.65
2	0.100	1.17
3	0.200	2.40
4	0.200	2.03
5	0.300	18.30
6	0.300	20.10
7	0.400	49.11
8	0.400	49.11

The number of mols of P_2O_5 in each sample was 49.11×10^{-6}. The filtrates from the first four samples were apparently normal. Samples 5 and 6 gave yellow filtrates and small yellow precipitates, while samples 7 and 8 gave no precipitates, but yellow solutions. Samples 7 and 8 were allowed to stand for twenty-four hours and a small precipitate formed in each, but no attempt was made to determine whether complete precipitation would result if a longer time were allowed.

OXALIC ACID

The authors have confirmed the work of Daniel and Griffin on the effect of oxalic acid on the precipitation of phosphorus as ammonium phosphomolybdate. However, all work seems to be only in qualitative agreement when precipitated in the presence of this organic compound. This is shown by the following results of analyses according to Procedure I.

Sample no.	Mols oxalic acid	Mols P_2O_5 not ppted. x 10^6
1	0.002	-0.26
2	0.002	0.19
3	0.004	-0.95
4	0.004	-1.45
5	0.006	-0.15
6	0.006	-0.64
7	0.008	48.12
8	0.008	48.12

The number of mols of P_2O_5 in each sample was 48.12×10^{-6}. The precipitates from samples 1 through 6 were apparently normal and the filtrates colorless. Samples 7 and 8 remained colorless and no precipitate formed. Sample 7 gave no precipitate on diluting with water and 8 gave no precipitate on standing overnight. It was found that the warming of a solution in which precipitation had been prevented by oxalic acid favored the formation of the precipitate. Thus when a sample similar

to 8 was warmed to thirty degrees centigrade, a precipitate formed. Larger amounts of oxalic acid did not completely prevent precipitation at higher temperatures. A sample similar to 8 gave a test for phosphates on the outside of the membrane when Procedure III was followed.

Several analyses were performed according to Procedure I except that 100 cc of molybdate solution instead of 50 cc were used, making the total volume 200 cc.

Sample no.	Mols oxalic acid	Mols P_2O_5 not ppted. x 10^6
1	0.0079	0.58
2	0.008	0.13

The number of mols of P_2O_5 in each sample was 48.12 x 10^{-6}. The filtrates were colorless and the precipitates were normal.

Reinbach and Wintgen[1] report the formation of a complex in a solution of molybdic and oxalic acid. In order to check the formation of a complex, the authors made a study of the lowering of the freezing point of solutions of sodium molybdate and oxalic acid. The data for the mixed solution is given below and that for the sodium molybdate alone is given on page 20.

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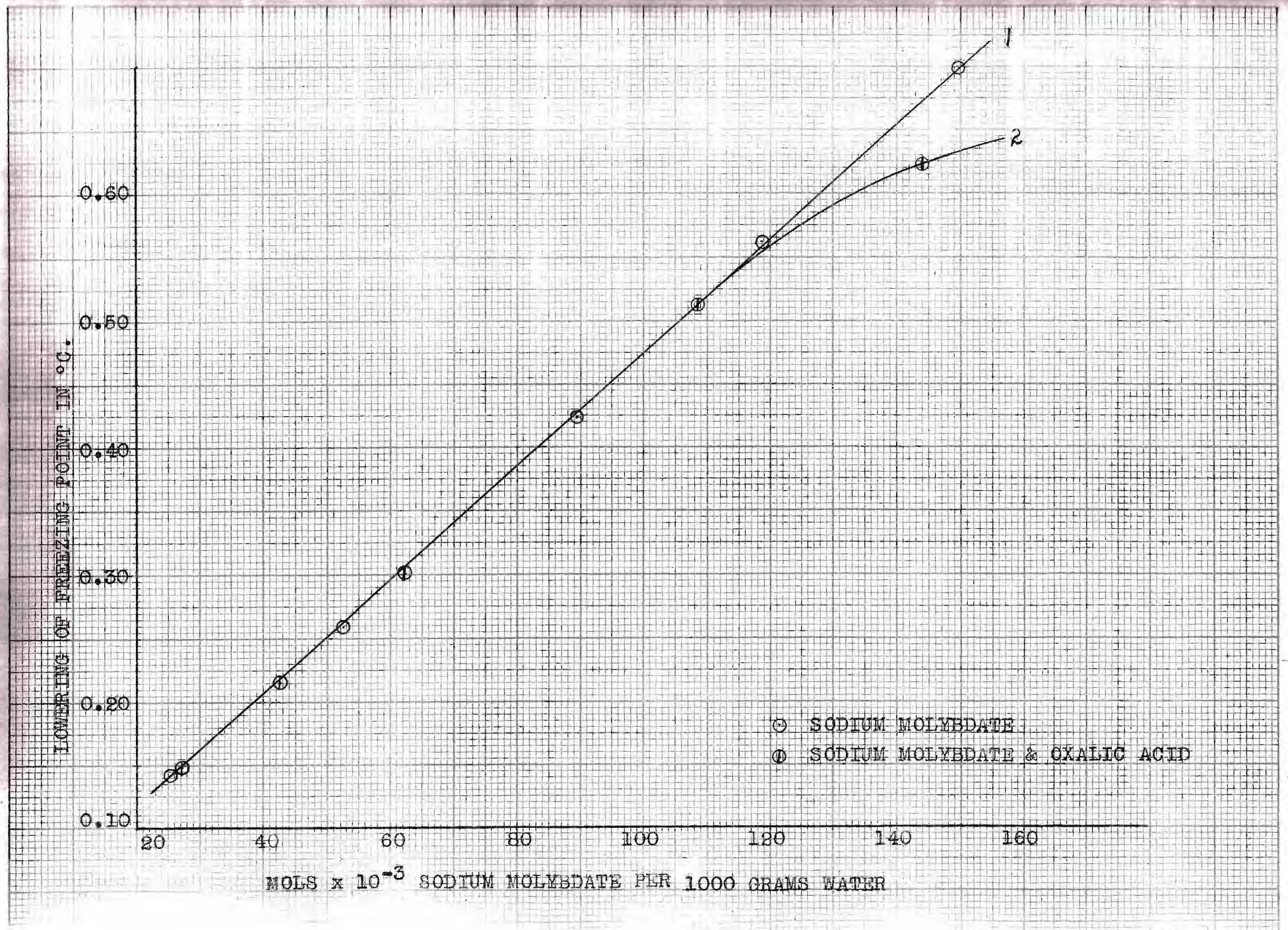
1) Loc. Cit.

Mols sodium molybdate	Mols oxalic acid	Lowering of F. P.
27.34×10^{-3}	23.60×10^{-3}	0.147
43.83	41.05	0.215
62.38	64.51	0.300
108.55	105.60	0.512
144.00	121.08	0.622

These values and those for sodium molybdate (page 20) are plotted on the following page. The upper curve (#1) represents the lowering of the freezing point of water by the addition of sodium molybdate, and is essentially a straight line. The other curve (#2) represents the lowering of the freezing point of water by the addition of the number of mols of sodium molybdate as shown and an approximately equal number of mols of oxalic acid. This curve indicates that the addition of oxalic acid does not increase the lowering and thus does not increase the number of particles in solution. This is suggestive of complex formation in the solution. A complex containing one molecule of sodium molybdate and one of oxalic acid would account for such a curve. The decrease in the lowering from that of sodium molybdate toward the end of the curve may be due to a complex containing one molecule of oxalic acid and two molecules of sodium molybdate, since this compound was added in excess.

Thus, the results of this study show that oxalic acid does prevent the precipitation of ammonium phosphomolybdate, probably by combining with the molybdate, thus reducing the


LOWERING OF FREEZING POINT IN °C.
0.60
0.50
0.40
0.30
0.20
0.10
20
40
60
80
100
120
140
160
MOLS x 10^{-3} SODIUM MOLYBDATE PER 1000 GRAMS WATER
1
2
⊙ SODIUM MOLYBDATE
◉ SODIUM MOLYBDATE & OXALIC ACID

concentration of this reagent. However, it is possible to precipitate the phosphorus almost completely by increasing the amount of molybdate solution.

CITRIC ACID

The following results were obtained according to Procedure II to show the effect of citric acid on the precipitation of phosphorus as ammonium phosphomolybdate. The results were similar to those of Daniel and Griffin.

Sample no.	Mols citric acid	Mols P_2O_5 not ppted x 10^6
1	0.002	1.24
2	0.004	1.48
3	0.006	1.29
4	0.008	6.94
5	0.010	45.55
6	0.0114	48.12

The number of mols of P_2O_5 in each sample was 48.12×10^{-6}. Similar results were obtained using other concentrations of citric acid, and even identical amounts produced small discrepancies of about the magnitude of those above. The precipitates which formed were apparently normal and the filtrates were colorless. As small precipitate formed in the filtrate from 4 and larger ones in samples 5 and 6 on the addition of molybdate solution.

Several analyses were carried out according to Procedure I except that 100 cc of molybdate solution instead of 50 cc were used, making the total volume 200 cc. The results were:

Sample no.	Mols citric acid	Mols P_2O_5 not ppted.x10^6
1	0.0114	1.09
2	0.0114	1.34

The number of mols of P_2O_5 in each sample was 48.12×10^{-6}. The precipitates appeared normal and the filtrates were colorless. The addition of molybdate solution to the filtrates gave no precipitation.

It was found impossible to effect a separation by means of a porous filter crucible or a dialysis membrane of a solution in which the precipitation had been prevented by citric acid. Furthermore, the solution in the outer tube gave a test for phosphates showing that this ion had passed through the membrane. These solutions differed from the yellow solutions in that they appeared free of yellow particles when examined under the microscope.

Reinbach and Wintgen[1] report the formation of a complex in a solution of molybdic acid and citric acid. A study was made of the lowering of the freezing point of solutions of sodium molybdate and citric acid in order to determine if a complex were formed. The data for the mixed solution are given below and that for the sodium molybdate alone is given on page 20.

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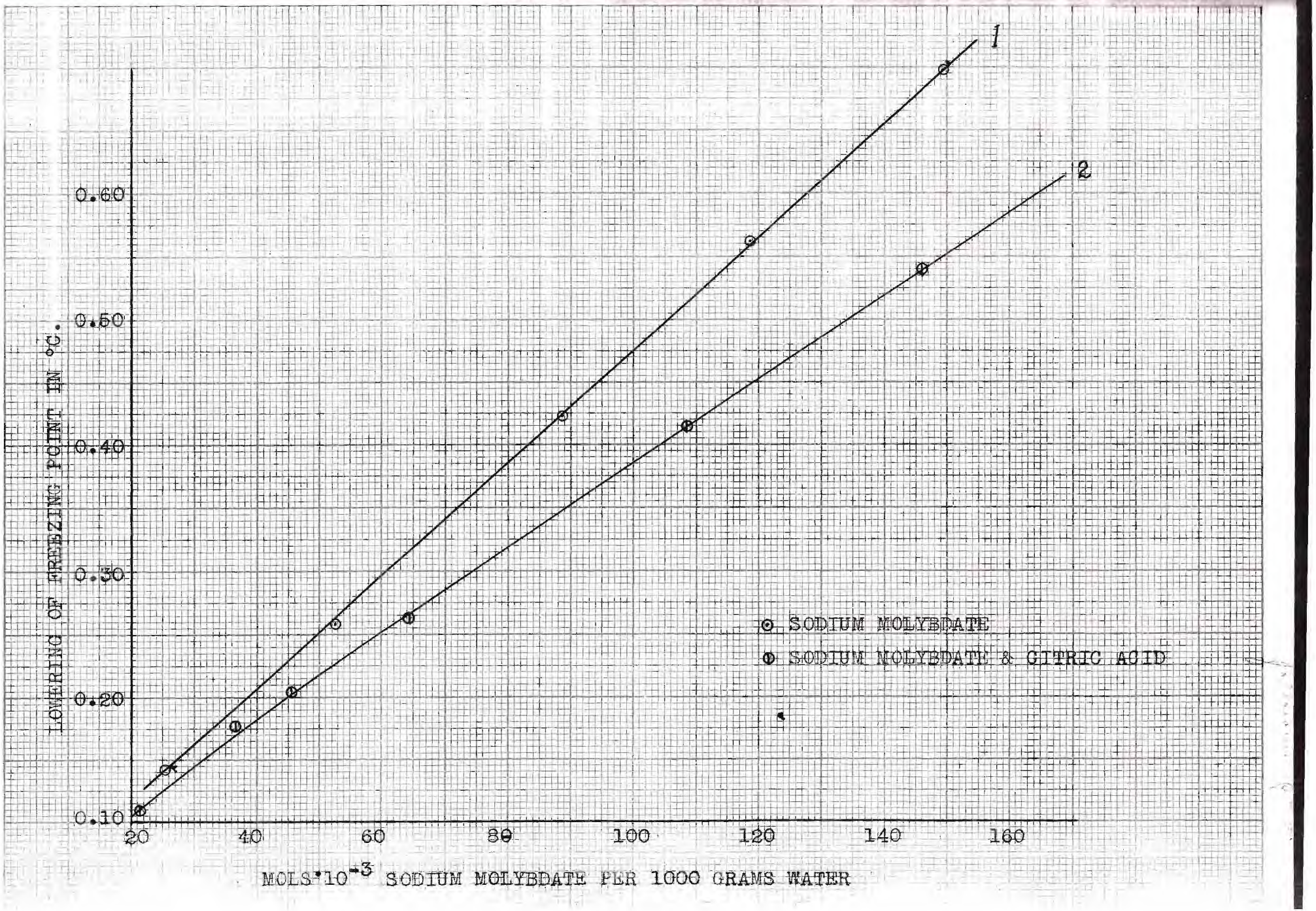
1) Loc. Cit.

Mols sodium molybdate	Mols citric acid	Lowering of F. P.
21.38×10^{-3}	24.73×10^{-3}	0.110
36.66	36.95	0.177
45.44	47.93	0.205
64.40	59.97	0.263
108.42	117.74	0.415
146.70	158.50	0.540

These values and those for sodium molybdate are plotted on the following page. The upper curve (#1) represents the lowering of the freezing point of water by the addition of sodium molybdate, and is essentially a straight line. The lower curve (#2) represents the lowering of the freezing point of water by the addition of the number of mols of sodium molybdate as shown and an approximately equal number of mols of citric acid. This curve shows that the addition of an approximately equal molal quantity of citric acid to a solution of sodium molybdate actually decreases the lowering of the freezing point. This seems to indicate that a complex is formed of which the degree of ionization is less than that of the sodium molybdate.

It was found that the amount of citric acid required to completely prevent the precipitation of ammonium phosphomolybdate was dependent on the temperature of the solution. Thus, the data already given show that 0.0114 mols of citric acid will prevent the precipitation in a solution containing 48.12×10^{-6} mols of P_2O_5 when only 50 cc of molybdate solution are used. However, a precipitate will form if the temperature is


1
2
0.60
0.50
0.40
0.30
0.20
0.10
LOWERING OF FREEZING POINT IN °C.
20
40
60
80
100
120
140
160
MOLS·10⁻³ SODIUM MOLYBDATE PER 1000 GRAMS WATER
SODIUM MOLYBDATE
SODIUM MOLYBDATE & CITRIC ACID

increased to 35 degrees centigrade. The addition of 0.0288 mols of citric acid will not prevent precipitation at seventy degrees centograde.

Thus, the results of this study show that citric acid does prevent the precipitaion of ammonium phosphomolybdate, probably by forming a complex with the molybdate and reducing the concentration of this reagent. However, if such a complex is formed, it becomes unstable as the temperature is increased, dissociating into the original products. It was also found that the ammonium phosphomolybdate could be almost completely precipitated by increasing the amount of molybdate solution.

TARTARIC ACID

The following results show the effect of tartaric acid on the precipitation of phosphorus as ammonium phosphomolybdate when analyzed according to Procedure I.

Sample no.	Mols tartaric acid	Mols P_2O_5 not ppted.x10^6
1	0.002	0.51
2	0.002	0.94
3	0.004	0.76
4	0.004	1.03
5	0.008	1.11
6	0.008	1.38
7	0.010	1.24
8	0.010	1.36
9	0.015	2.08
10	0.020	17.96
11	0.0266	52.81

The number of mols of P_2O_5 in each sample was 52.81×10^{-6}. Each precipitate was normal in appearance and the filtrates were colorless. Molybdate solution was added to each of the filtrates from samples 1 through 10, but only 10 produced a precipitate. Sample 11 did not give a precipitate, but on the addition of more molybdate solution the yellow precipitate formed. A sample similar to 11 gave no precipitate on dilution

to 400 cc with distilled water.

Several samples were analyzed according to Procedure I except that 100 cc of molybdate solution were used instead of 50 cc, making a total volume of 200 cc. The results were as follows:

Sample no.	Mols tartaric acid	Mols P_2O_5 not ppted.x10^6
1	0.0266	0.45
2	0.0266	0.67

The number of mols of P_2O_5 in each sample was 48.12×10^{-6}. The precipitates appeared normal and the filtrates were colorless. The addition of molybdate solution to the filtrates did not give a precipitate.

Unsuccessful attempts were made to demonstrate the presence of colloidal ammonium phosphomolybdate according to Procedure III and IV. A test was obtained for phosphates on both sides of the membrane when dialysis was attempted.

Reinbach and Wintgen[1] report the formation of a complex in a solution of molybdic acid and tartaric acid. The results of this study also indicate the formation of a complex in the solution thus preventing the precipitation of the ammonium phosphomolybdate. However, if a complex is formed which reduces the concentration of the molybdate ion in the solution, dissociation occurs at higher temperature, as shown by results similar to those obtained with citric acid.

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1) Loc. Cit.

These results indicate that tartaric and citric acid have the same effect on the precipitation of phosphorus as ammonium phosphomolybdate.

LACTIC ACID

The following results were obtained according to Procedure I in a study of the effect of lactic acid on the precipitation of phosphorus as ammonium phosphomolybdate:

Sample no.	Mols lactic acid	Mols P_2O_5 not ppted. $\times 10^6$
1	0.020	1.45
2	0.020	1.13
3	0.040	2.23
4	0.040	1.90
5	0.060	1.67
6	0.060	2.23
7	0.080	1.24
8	0.080	2.11
9	0.100	10.19
10	0.100	10.88
11	0.120	48.11
12	0.120	48.11

The number of mols of P_2O_5 in each sample was 48.11×10^{-6}. Additional samples were run containing larger amounts of lactic acid, but similar colorless solutions with no precipitates were obtained. All of the filtrates from the samples were colorless, and the addition of potassium nitrate solution (wash water) produced no change. However, a precipitate formed in sample 12 on the addition of molybdate solution.

Several analyses were performed according to Procedure I except that 100 cc of molybdate solution instead of 50 cc were used, making a total volume of 200 cc. The results were as follows:

Sample no.	Mols lactic acid	Mols P_2O_5 not ppted.x10^6
1	0.120	1.26
2	0.120	2.13

The number of mols of P_2O_5 in each sample was 48.11×10^{-6}. The filtrates from these samples were colorless and did not give a precipitate on the addition of molybdate solution.

The results of analysis according to Procedure III and IV were similar to those with citric acid.

Lactic acid is similar to citric and tartaric acid in that a larger amount is required to prevent the precipitation at a higher temperature.

Reinbach and Wintgen[1] report the formation of a complex in a solution of molybdic acid and lactic acid which further indicates that this acid affects the precipitation of ammonium phosphomolybdate in a manner similar to citric acid.

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1) Loc. Cit.

GLYCOLIC ACID

Daniel and Griffin have shown that this organic compound will completely prevent the precipitation of ammonium phosphomolybdate. This is verified by the following results by the authors:

Sample no.	Mols glycolic acid	Mols P_2O_5 not ppted.x10^6
1	0.020	0.44
2	0.020	0.32
3	0.050	0.55
4	0.050	0.07
5	0.100	0.65
6	0.100	0.86
7	0.150	23.48
8	0.150	23.90
9	0.160	48.11
10	0.160	48.11

The number of mols of P_2O_5 in each sample was 48.11×10^{-6}. The filtrates from each of the first eight samples were colorless. However, on the addition of molybdate solution to each of these filtrates, only 7 and 8 gave a precipitates, A precipitate formed in sample 9 on the addition of molybdate solution, but the addition of water to sample 10 produced no effect.

Several samples were analyzed according to Procedure I except that 100 cc of molybdate solution instead of 50 cc were used (making a total volume of 200 cc of solution). The results were as follows:

Sample no.	Mols glycolic acid	Mols P_2O_5 not ppted.x10^6
1	0.164	0.60
2	0.164	0.41

The number of mols of P_2O_5 in each sample was 48.11 x 10^{-6}. The addition of molybdate solution to filtrate 1 and water to filtrate 2 did not give a precipitate.

The results of analysis according to Procedure III and IV were similar to those with citric acid.

The effect of glycolic acid on the precipitation of phosphorus as ammonium phosphomolybdate is similar to that of citric acid in that larger amounts are required to prevent the precipitation at higher temperatures.

Reinbach and Wintgen[1] report the formation of a complex in a solution of molybdic acid and glycolic acid. This further indicates that glycolic acid affects the precipitation of ammonium phosphomolybdate in a manner similar to citric acid.

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1) Loc. Cit.

DISCUSSION OF RESULTS

This study of the effect of organic matter on the precipitation of phosphorus as ammonium phosphomolybdate is far from complete. The work of the authors, however, verifies that of Daniel and Griffin in that a large number of organic compounds does affect this precipitation.

When precipitation of ammonium phosphomolybdate is prevented by organic compounds (only a relatively small number are here included), either a colorless or yellow solution results. Evidence indicates that there are distinct differences between the interferences of the two types of compounds producing these results.

Those organic compounds, such as acetic acid, propionic acid, etc., which produce a yellow solution on the addition of the ammonium molybdate, merely retard the precipitation of the ammonium phosphomolybdate. However, this retardation occurs to such an extent in the presence of large amounts of these compounds, that precipitation is completely prevented in the short time allowed in the official method of analysis. The exact nature of the interference is unknown, but results of this study indicate that these organic compounds have a stabilizing action on the ammonium phosphomolybdate, thus forming a colloidal sol which cannot be separated by ordinary filtration. Evidence in favor of this includes: (1) increase of precipi-

tation by the addition of an electrolyte; (2) increase of precipitation on standing; (3) increase of precipitation on dilution with water; (4) separation of the yellow precipitate from the yellow solution by dialysis; and (5) observation of small yellow particles when the yellow solutions are examined under the microscope.

The results of this investigation show that small amounts of these organic compounds also produce a disturbing effect. Most of them produce an apparent increase in precipitation, but a few such as propionic acid give low values. Perhaps an explanation can be found by determining the composition of the ammonium phosphomolybdate which is formed in the presence of organic compounds. The increase in precipitation may be due to occluded molybdic acid which is not removed by washing with the potassium nitrate solution. On the other hand, a possible explanation for the low values is the formation of a compound which contains less molybdic acid than represented by the true formula of ammonium phosphomolybdate.

There are also those organic compounds which not only prevent the precipitation, but produce a colorless solution. To this type belong oxalic acid and the hydroxy acids - glycolic, lactic, tartaric, and citric. However, it was found that increasing the amount of molybdate solution would give a precipitate, but the results were always slightly low. There seems to be a relation between the amount of the organic compound (oxalic acid or hydroxy acid) present and the amount of

molybdate required for precipitation. This indicates the formation of a complex compound which removes the molybdic acid from solution. The work of Reinbach and Wintgen and that of the authors show that such complexes will form in water solution. Thus the same phenomenon probably occurs in the nitric acid solution from which it is desired to precipitate the ammonium phosphomolybdate. The formation of such complexes removes the precipitating reagent from the solution preventing the formation of the ammonium phosphomolybdate. Hence, the addition of more molybdate solution will give a precipitate.

In the procedure used for the determination of phosphorus as ammonium phosphomolybdate, the amount of ammonium molybdate added was approximately twelve times the amount actually required in the formation of the compound. Other procedures recommend correspondingly large amounts. The following results were obtained in order to show the effect of varying the amount of molybdate used.

Sample no.	cc molybdate sol'n used	Mols P_2O_5 not ppted.x10^6
1	25.00	1.51
2	25.00	1.62
3	5.00	2.82
4	5.00	3.54

The number of mols of P_2O_5 in each sample was 48.11×10^{-6}, based on complete precipitation with the addition of 50 cc of molybdate solution. The addition of molybdate solution to

the filtrates did not give a precipitate, indicating that all of the phosphates had been precipitated. Thus, if the hydroxy acid removes the molybdate from the solution with the formation of a complex, this would account for the low values obtained when the ammonium phosphomolybdate was precipitated in the presence of one of these acids. Analyses of several samples precipitated in the presence of citric or tartaric acid indicate this, but due to insufficient data definite conclusions cannot be drawn.

SUMMARY

This investigation confirms that of Daniel and Griffin that organic matter affects the precipitation of phosphorus as ammonium phosphomolybdate.

Certain organic compounds such as acetic acid retard the precipitation, probably due to a stabilizing action of the ammonium phosphomolybdate.

Other organic compounds such as oxalic acid and some of the hydroxy acids apparently form complexes with the molybdate ion or molybdic acid, thus reducing the concentration of this reagent.

Evidently, there are other interference phenomena which produce discrepancies in the presence of small amounts of organic matter.